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ASSESSMENT OF MAIN MINERAL WATER ROMANIAN MARKS FROM THE PERSPECTIVE OF SOME TOXICOLOGICAL PARAMETERS

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Abstract

*The paper aimed to analyze 15 Romanian brands of mineral waters and in this purpose therey were bought from a hypermarket. The content of nitrates, nitrites and pH have been determined for each of the 15 mineral waters using the modern known techniques. A number of two-thirds (66.67%) of the producers did not specify the nitrates content of mineral waters on the label. The firms which mentioned the content of nitrates on the label have not been correct as the tested value of nitrates was higher than the one stated on the label. The mean of nitrates in the tested mineral waters was 5.89 ± 2.88 mg/l, well below the maximum limits (50 mg/l). The fact that most producers do not specify the mineral waters nitrites content, this is not a health issue for consumers, because the research results showed that the presence of nitrites in the Romanian mineral waters is extremely low, somewhere besides the detection limits of the analytical method used. The nitrites content of tested mineral waters was significantly lower in waters with a greater pH. In fact, the increasing the pH of mineral waters by one unit, determined the reducing of nitrites amount by about 32% (r = 0.57 *). As a practical conclusion, consumers could use this criterion in choosing the type of water they want to drink.*

Key words*: nitrates, nitrites, pH mineral waters*

INTRODUCTION

There is at least an advertising campaign of some mineral waters companies in the local market, which insists on the purity of the mineral waters. The term "purity" of a water has a series of connotations that makes it difficult to define. The expression "the purest mineral water in the world" remains an empty word if there is no predefined standard for this purity. For example, by their very nature, mineral waters are not pure compared with the purest water, namely distilled water.

Consumption of mineral waters is based precisely on their ability to provide a range of essential salts for the purposes of metabolic processes smooth running. From this perspective, the purity of mineral waters is certainly a defect. We are interested in the mineral waters to be microbiologically pure, since the presence of some microorganisms threaten our health. At the same time, we are interested in the waters to be free of nitrites or nitrates, because of the toxigenic potential.

On the other hand, each of us have different needs in terms of water consumption. People with kidney stones seek oligo-alkaline waters. People with cardiovascular disease seek low-sodium mineral waters, possibly rich in magnesium and calcium etc. Therefore, the most appropriate term to characterize a mineral water, in terms of all categories of potential consumers is a classic one, used to characterize all products from the food industry, namely inocuity.

Inocuity represents a quality of a product to be not harmful to consumers [2]. Besides air, water is the substance through which the body performs most intense exchanges with the environment. The recommended daily intake of water (30-40 ml / kg) makes it an important element in achieving a healthy lifestyle [3].

In order to assess inocuity in the case of mineral waters, we tested 15 samples of mineral waters, in terms of nitrites (NO_2^-) and nitrates (NO_3^-) content. A further determination of relevance for certain

categories of consumers was water pH.

MATERIALS AND METHODS

In the first week of March 2014, 15 samples of mineral waters produced by 15 Romanian brands, were bought from Auchan supermarket in Titan Shopping Center (Bucharest). The type of mineral water, its source and producer names are shown in Table 1.

Table 1. Mineral water brand names and main key identifiers

No. sample	Commercial name	Source	Producer
P1	Bucovina uncarbonated	C7 SECU, Dorna Candrenilor, Suceava	Rio Bucovina SRL
P2	Bilbor	Q1, Bilbor, Harghita county (height rate 1114, Călimani mountains)	Bilbor Mineral Water SRL
P3	Zizin	F2, F4, Zizin, Braşov county	Apemin Zizin S.A.
P4	Dorna - Izvorul alb	White spring, Dealul Floreni -Dorna Candrenilor village, Suceava county	Coca Cola HBC SRL
P5	Apa Craiului	Spring water no. 5, Gâlgoaie, Dâmbovicioara, Argeş county	Cheresta Dîmbovicioara SRL
P6	Aqua Carpatica	Băjenaru spring, Păltiniş, Suceava county	Carphatian Springs S.A.
P7	Keia uncarbonated	Zăganului spring, Ciucaş, Prahova county	Nicoltana S.A.
P8	Perenna Premier uncarbonated	Călina, Caraş Severin county	Apollini Company SRL
P9	Cheile Bicazului	Bicazul Ardelean (drilling FH1), Neamţ county	Natural Aqua Group SRL
P10	Borsec uncarbonated	Făget Borsec, Harghita county	Romaqua Group S.A.
P11	Herculane uncarbonated	Domogled, Băile Herculane, Caraş Severin county	Carpatina S.A.
P12	Carpatina light mineral	Toşorog, Neamţ county	Carpatina S.A.
P13	Perla Covasnei	F1, Târgu Secuiesc, Covasna county	Covasn pearl S.A.
P14	Hera	Hera, Budureasa, Bihor county	European Drinks
P15	Tuşnad Spring fairy	Tuşnad, Harghita county	Apemin Tuşnad S.A.

The content of nitrates, nitrites and pH was determined for each of the 15 tested mineral waters.

The acid fenoldisulfonic reaction method was used to determine the concentration of nitrates. In this purpose, the formation of a yellow nitrofenolsulfonic derivative was needed to be involved. This substance had the photometrically determined intensity, at 480 nm, proportional to the nitrates content in the sample [4].

Saltzman method was usedto determine the Nitrites content. The method made use of the property of nitrite ions to form, through a chemical reaction, a colored azo complex that can be photometrically evaluated.

Ther nitrite ions react with sulfanilic acid in an acid medium to form a diazonium salt, which, in its turn, is coupled with N-naphthyl ethylenediamine, at pH = 2-2.5, to form a violet azo compound, whose absorbance is measured at a wavelength of 520 nm [4].

A digital pH-meter was used to determine pH. The pH varies at the variation of the potential difference between a glass electrode and a reference electrode, placed in the water sample to be analyzed [4].

RESULTS AND DISCUSSIONS

The nitrites, nitrates contents and pH, in the tested samples used in this study and written on the labels of mineral waters samples are comparatively shown comparatively in Table 2.

From Table 2, it can be seen that the tested mineral waters had a pH range of variation between 6.4 and 7.8. This coincides partly with the range of variation recorded on the tested mineral waters labels (5.76 to 7.83).

On uncarbonated waters Bilbor, Hera and Tusnad labels the pH is not specified, so that its value did not enter into our calculation, but the first two mineral waters (Bilbor and Hera) had slightly alkaline pH (pH 7.4) and Tusnad mineral water was slightly acid (pH = 6.8).

The tested mineral waters mean value of pH was 7.37 ± 0.42 (n = 15), higher than that recorded on the appropriate labels, respectively pH = 7.25 ± 0.56 (n = 12).

Table 2. pH, nitrites (NO_2^-) and nitrates (NO_3^-) content in mineral waters

No. Sample	Declared/ tested	pH, T^0C	Nitrites (NO_2^-) mg/l	Nitrates (NO_3^-) mg/l
P1	declared	7.05	< 0.01	4.71
	Tested	7.7 (22.2°C)	0.014	5.420
P2	declared	-	-	-
	tested	7.4 (23.3°C)	0.023	4.700
P3	declared	7.4	< 0.003	-
	tested	6.7 (23.3°C)	0.023	7.580
P4	declared	7.49	-	4.13
	tested	7.6 (23.3°C)	0.019	5.840
P5	declared	7.57	-	-
	tested	7.6 (23.3°C)	0.020	6.060
P6	declared	7.7	-	1.85
	tested	7.7 (23.3°C)	<LOQ	3.500
P7	declared	7,83	-	-
	tested	7.8 (23.4°C)	<LOQ	7.400
P8	declared	7.29	< 0.003	2.1
	tested	7.4 (23.4°C)	<LOQ	3.980
P9	declared	7.6	-	-
	tested	7.3 (23.4°C)	<LOQ	14.60
P10	declared	7,43	-	-
	tested	7.5 (23.4°C)	<LOQ	4.580
P11	declared	7.25	-	-
	tested	7.7 (23.5°C)	<LOQ	4.680
P12	declared	6,65	-	-
	tested	6.4 (23.5°C)	0.023	6.100
P13	declared	5.76	-	< 0.083
	tested	7.0 (23.5°C)	0.023	2.260
P14	declared	-	-	-
	tested	7.4 (23.5°C)	0.021	3.800
P15	declared	-	-	-
	tested	6.8 (23.5°C)	0.020	7.800

LOQ for NO_2^- = 0.014 ppm (The detection limit of the method, very significant); LOQ for NO_3^- = 1.306 ppm

The difference between mean values of pH was not statistically significant (Student test value was t = 0.55) (Fig.1).

We also observed that there are differences between the tested pH values and those recorded on the labels. The most obvious of these was the case of water Perla Covasnei (with an extra of 1.24 pH units from the label).

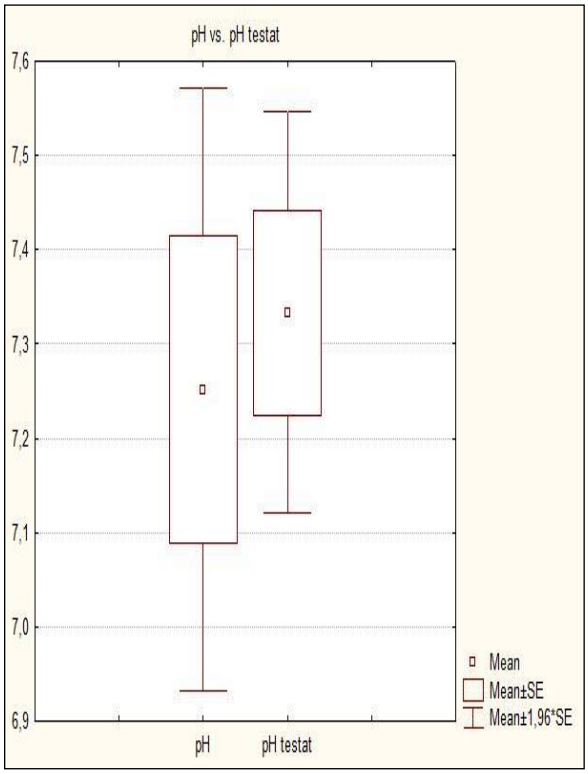

Fig. 1. Comparison between the mean values of pH (tested and recorded on the labels)

Large deviations were observed for Bucovina, Zizin and Herculane waters (figure 2). For Bucovina, Zizin and Perla Covasnei, the differences are large enough to declassify those mineral waters in the pH range suggested by the labels.

Thus, Bucovina alkaline water is presented as neutral, acidic Zizin water is presented as alkaline and neutral Perla Covasnei water is presented, according to the label, as acidic.

Mineral waters can be, under certain conditions, important sources of nitrites and nitrates. Most of the producers tend to minimize the mineral waters contribution to daily exposure to substances with toxigenic potential, but the phenomenon is not insignificant.

Mineral waters consumed in recommended amounts (30-40 ml/kg) might be important sources of exposure, where consumers are already exposed to these substances via daily diet (fruits, vegetables, and meat products).

From table 2 we can see that a number of two-thirds (66.67%) of the producers did not specify the content of mineral waters in nitrates.

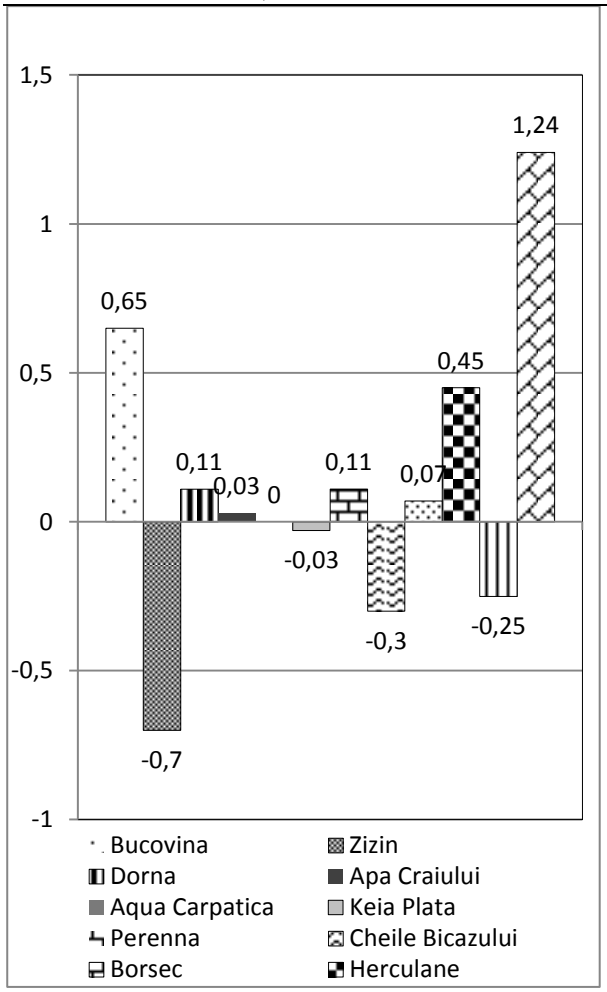

Fig. 2. Individual deviations of the mineral waters pH from the values recorded on the labels

Where this happens, the nitrates content tested value is much higher than that recorded on the label (Fig. 3).

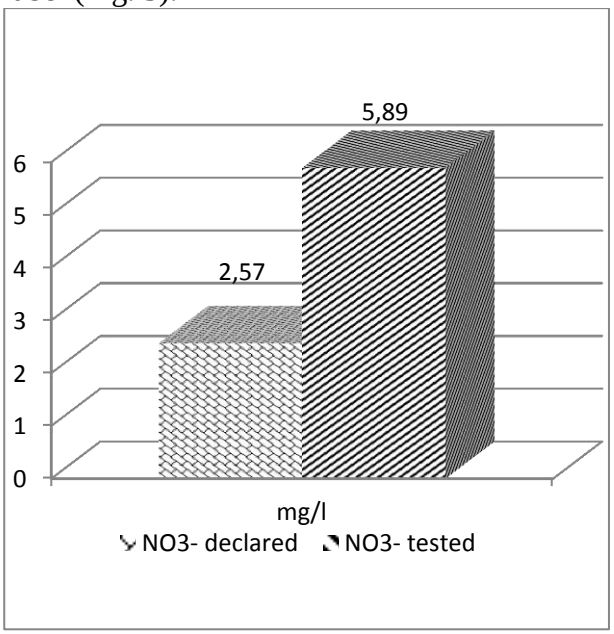

Fig. 3. Mean values of nitrates content in mineral waters

The mean showed 5.89 ± 2.88 mg/l. However, the nitrates content mean of mineral water samples was much lower than the limit imposed by the World Health Organization for drinking water (50 mg/l).

The largest amount of nitrates (14.6 mg/l) was observed in Bicaz mineral water and the lowest in Perla Covasnei water (2.26 mg/l).

There were no significant differences between regions, concerning the nitrates content in uncarbonated mineral waters.

The smaller amounts of nitrates were found in the Western region waters (4.15 ± 0.46 mg/l) and the largest quantities in the waters of the North (6.39 ± 3.72 mg/l) (Fig. 4).

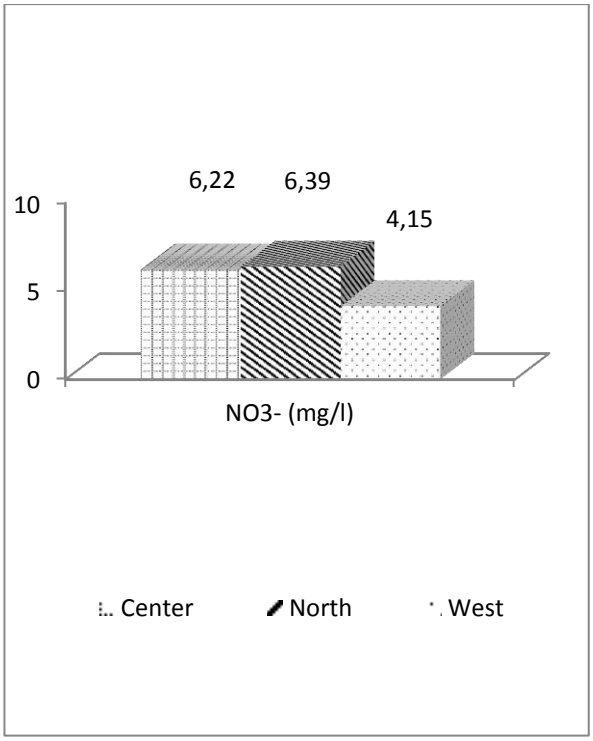

Fig. 4. The nitrates content main values in mineral waters, according to their origin

Table 2 shows that most of the producers did not specify on the labels the nitrites content of mineral waters.

However, the fact is not a problem, because our results showed that the presence of nitrites in uncarbonated mineral water was extremely low, somewhere next to the detection limits of the used analytical method.

Even the nitrites main obtained 0.012 ± 0.011 mg/l (n=15) was below the detection limit of the method.

This was due to the fact that for a number of 6

samples, representing 40% of the tested mineral waters, the nitrites content was below the limit of detection.
However, the nitrites content of tested mineral waters is well below the maximum limits of 0.5 mg/l, which makes the mineral waters in Romania to be safe for consumption.
The nitrites content of tested mineral waters was significantly lower in the waters with a higher pH (Fig.5).

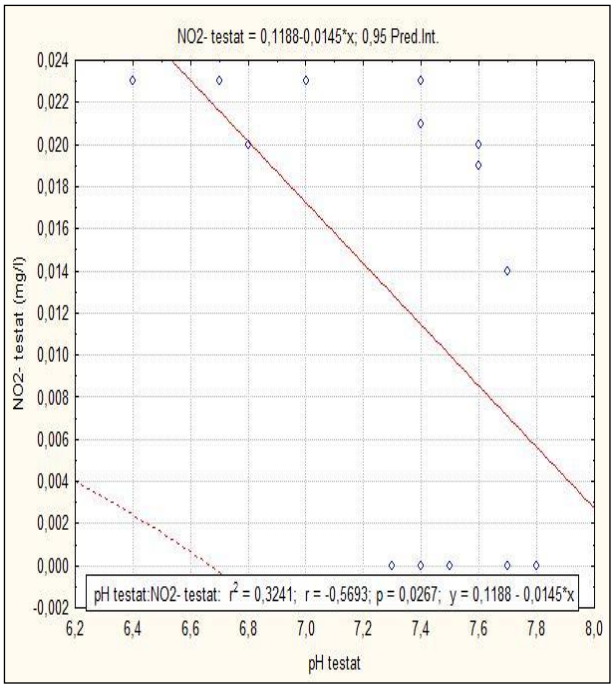

Fig. 5. Regression NO_2^- - pH for mineral waters

In fact, the raising of pH by one unit caused a decrease in the nitrites amount of about 32% (the coefficient of determination $r^2 = 0.32$). This can be a criterion to guide consumers in choosing the type of water.

CONCLUSIONS

Base on the analysis made on thse samples of mineral water, it was possible to draw several important conclusions.
The pH mean of the tested mineral waters was 7.37 ± 0.42, higher than that recorded on the labels (7.25 ± 0.56), but not significantly different.
The Perla Covasnei mineral water presented in addition 1.24 pH units from the value recorded on the label. Noticeable deviations were also observed for Bucovina, Zizin and Herculane mineral waters.
Large differences in pH declassified certain waters in the pH range suggested by the labels. Thus, the alkaline water Bucovina is presented as neutral, acidic water Zizin is presented as alkaline and neutral Perla Covasnei is presented as acidic.
Two thirds (66.67%) of the producers did not specify on the labels the nitrates content of mineral waters. Where this happens, the nitrates content tested values were much higher than that recorded on the labels.
Real nitrates content mean of tested mineral waters was 5.89 ± 2.88 mg/l, well below the maximum limits (50 mg/l).
Most of the producers did not specify on the labels the nitrites content of mineral waters. In 40% of mineral waters, which had the nitrites content specified on the labels, it was found that it was below the detection limit.
The nitrites content of mineral waters was significantly lower in waters with a greater pH. The raising of pH by one unit caused a decrease in the nitrites amount of about 32% (r = 0.57 *). This phenomenon can be a criterion to guide consumers in choosing the type of water.

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